Molecular Interaction in Mixtures of Dioxane and Chloroform

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THE SYSTEM dioxane-chloroform has been studied in the liquid state by measurements of vapor pressures and heats of mixing (*3*) and by determination of molar polarization (*1*). The present investigation aimed to ascertain whether compounds AB and AB_2 mentioned in these publications or any other compounds exist in the solid state.

EXPERIMENTAL

Materials. DIOXANE. It was purified by refluxing it for 12 hours with 1*N* hydrochloric acid, while a slow stream of nitrogen was passed. The product was treated with potassium hydroxide and subsequently refluxed with sodium metal. The dioxane was then fractionally crystallized and further subjected to fractional distillation over sodium. The freezing point of the sample was 11.8°–11.6° C.

CHLOROFORM. Chloroform (analytical reagent grade) was shaken with distilled water several times to remove ethyl alcohol. It was dried over fuzed calcium chloride for 48 hours and then distilled over phosphorus pentoxide. Anhydrous sodium carbonate was added to the distillate to remove the acidity and it was fractionally distilled. The freezing point of the sample was −63.4° C.

Procedure. The method of thermal analysis was similar to that adopted by Rastogi and Nigam (*5*). However, three modifications were made. The design of the thermal analysis cell was changed so that condensation of moisture was avoided during stirring. A thermistor was used for measuring temperatures. The cooling bath consisted of either liquid air or a mixture of liquid air and alcohol. For this purpose an unsilvered Dewar flask was used in order to determine the amount of liquid air in the Dewar flask at any time. The modified thermal analysis cell is shown in Figure 1.

Tube *A* had a stirrer, *D*, with a mercury seal and *A* was connected to tube *B* by a standard ground glass joint. The temperature-measuring device was introduced through tube *C*, which was tightly corked. This arrangement helped the stirring of the mixture in tube *B* without introducing any moisture. Tube *B* was kept in a double-walled tube which was connected to the vacuum line. The maximum uncertainty in temperature measurement was of the order of ±0.05° C.

The experimental results for the chloroform-dioxane mixture are recorded in Table I and plotted in Figure 2.

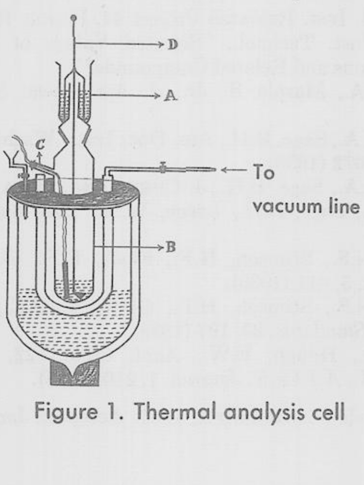


Figure 1. Thermal analysis cell

Table I. Chloroform-Dioxane Mixture

Dioxane, Mole Fraction	F.P., ° C.	Thaw Point, ° C.
0.0000	−63.4	...
0.0947	−64.6	−70.8
0.1444	−67.0	−70.8
0.2004	−65.5	−70.8
0.2970	−57.5	...
0.3329	−57.3	...
0.3877	−51.3	−58.1
0.4486	−32.8	−57.8
0.5083	−28.7	−58.1
0.5610	−22.5	−28.9
0.6064	−17.3	−29.1
0.6964	−7.9	−30.1
0.7909	−0.95	−19.9
0.8688	3.4	−1.4
0.9192	6.6	−1.0
0.9421	8.1	−1.0
1.0000	11.6	0.5- −0.8

DISCUSSION

From Figure 2, it is clear that both AB and AB_2 are formed in mixtures of dioxane and chloroform. The former has an incongruent melting point. This system had been earlier studied by Kennard and McCusker (*2*), but since they did not determine the thaw points, no great reliance can be placed on the phase diagram obtained by them. Determination of the thaw points is sometimes very useful in broadly confirming the nature of the phase diagram. This is precisely the reason why they missed the incongruently melting compound. The phase diagram proves the following for (A = dioxane, B = chloroform):

Compound AB_2 exists in the solid state.

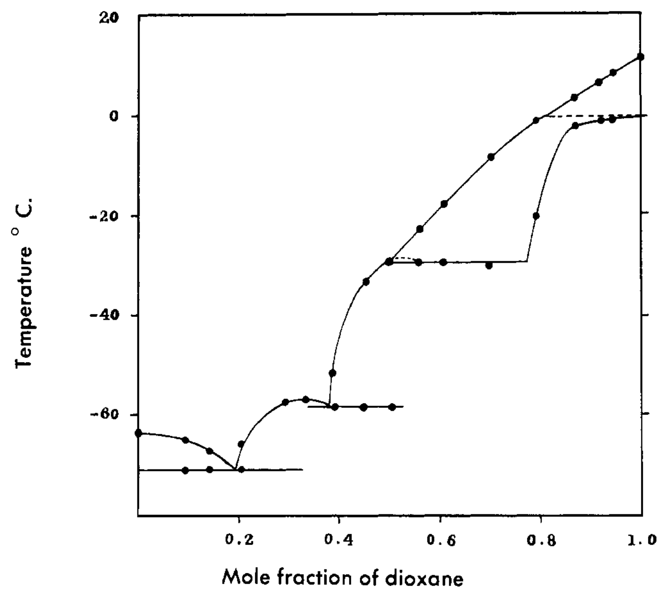
Compound AB exists in the solid state, but only below the incongruent melting point.

However, it is difficult to ascertain whether these compounds exist in the liquid state in appreciable amounts. The observed data between the region of the two eutectics are best fitted by an equation of the type:

$$-2.303 \log_{10}(x_A)^m(x_B)^n = K_1\left(\frac{1}{T} - \frac{1}{T_c}\right) + K_2$$

where x_A and x_B are the stoichiometric mole fractions of A and B in the liquid phase and T is the temperature in ° K. T_c is the congruent melting point of the compound $A_mB_n \cdot K_1$ and K_2 are the constants; m and n are integers. Figure 3 shows that a relationship of the above type is obeyed by both complexes. The value of K_1 for AB and AB_2 complexes is found to be 670° and 3280°, respectively.

The above equation is similar to that given by Prigogine and Defay (*4*). K_1 can be identified with $h_{T,P}/R$ where $h_{T,P}$ is the heat of fusion and R is the gas constant, provided the species behaves ideally and the actual mole fraction of A and B can be taken to be equal to their stoichiometric mole fractions. It is difficult to say whether the second condition would hold in such mixtures.



← Figure 2. Phase diagram of dioxane (A)-chloroform (B)

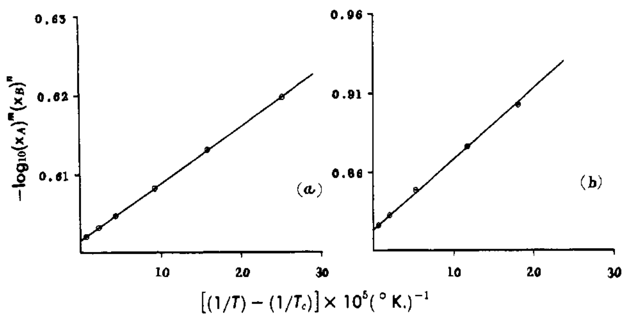


Figure 3. Estimation of heats of fusion
a. AB complex
b. AB_2 complex

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Density of Nitric Acid–Water Mixtures at Very Low Concentrations of Added Water

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THE DENSITY of nitric acid-water mixtures has been studied extensively and the results have been summarized in various places—for instance, in the International Critical Tables (*3*). However, detailed measurements have not been made at very low water concentrations in the region below 1% by weight.

Recently, the densities of solutions of ammonium nitrate and tetramethylammonium nitrate in nitric acid were measured (*2*). For both solutes, the density-composition curves at constant temperature showed features near 0.2 molal which were attributed to the onset of self-dissociation of the nitric acid in the generally accepted fashion (*3*):

$$2HNO_3 \rightleftarrows NO_2^+ + NO_3^- + H_2O \qquad (1)$$

It was of some interest, then, to determine whether the addition of water to nitric acid gave similar effects.

EXPERIMENTAL

The nitric acid used was prepared as described previously (*1*). The water used was freshly boiled and cooled laboratory distilled water.

Density was determined from the loss in weight of a Vycor sinker suspended from one arm of a balance by a platinum wire 0.003 inch in diameter. Sinkers were used which had volumes of about 5 and 14 cc. The sample cell, containing about 50 to 100 ml. of liquid, was immersed in a water bath whose temperature was constant to ±0.01° C. The cell was fitted with a ground-glass cap having a hole about 2.5 mm. in diameter in its top, through which the suspension wire passed.

In the course of a run, the density of the pure acid was measured; then water was added through the hole in the cap in small increments. After each increment, the cell was shaken manually with the sinker suspended in place, and the change in weight was recorded.

RESULTS AND DISCUSSION

Figure 1 shows results for the addition of water to nitric acid at 16.61° ± 0.01° C., data being taken at intervals of a few tenths weight percent up to about 3% water. Figure 2 shows results in much greater detail obtained at 17.83° and 32.29° ± 0.01° C., and up to a maximum water concentration of about 0.5% by weight. The data are plotted as